What is claimed is:

1. A zinc-free glass frit comprising, by weight, from about 50% to about 70% SiO_2, from about 5% to about 20% CaO, from about 3% to about 15% Al_2O_3, up to about 20% BaO, up to about 15% B_2O_3, up to about 10% K_2O, up to about 6% Na_2O, up to about 10% ZrO_2, up to about 5% MgO and up to about 5% PbO.

2. The zinc-free glass frit according to claim 1 comprising, by weight, from about 52.0% to about 64% SiO_2, from about 8% to about 15% CaO, from about 4% to about 11% Al_2O_3, from about 7% to about 15% BaO, up to about 13% B_2O_3, from about 2% to about 8% K_2O, up to about 4% Na_2O, up to about 8% ZrO_2 and up to about 3% MgO.

3. The zinc-free glass frit according to claim 1 comprising, by weight, from about 53% to about 61% SiO_2, from about 10% to about 12% CaO, from about 5.5% to about 9% Al_2O_3, from about 8% to about 12% BaO, up to about 12% B_2O_3, from about 3.5% to about 6% K_2O, up to about 2% Na_2O, up to about 8% ZrO_2 and up to about 2% MgO.

4. A glaze composition for forming a glossy protective surface on ceramic architectural tile, the glaze composition comprising a zinc-free glass frit, the zinc-free glass frit comprising, by weight, from about 50% to about 70% SiO_2, from about 5% to about 20% CaO, from about 3% to about 15% Al_2O_3, up to about 20% BaO, up to about 15% B_2O_3, up to about 10% K_2O, up to about 6% Na_2O, up to about 10% ZrO_2, up to about 5% MgO and up to about 5% PbO.

5. The glaze composition according to claim 4 wherein the zinc-free glass frit comprises, by weight, from about 52% to about 64% SiO_2, from about 8% to about 15% CaO, from about 4% to about 11% Al_2O_3, from about 7% to about 15% BaO, up to about 13% B_2O_3, from about 2% to about 8% K_2O, up to about 4% Na_2O, up to about 8% ZrO_2 and up to about 3% MgO.

6. The glaze composition according to claim 4 wherein the zinc-free glass frit comprises, by weight, from about 53% to about 61% SiO_2, from about 10% to about 12% CaO, from about 5.5% to about 9% Al_2O_3, from about 8% to about 12% BaO, up to about 12% B_2O_3, from about 3.5% to about 6% K_2O, up to about 2% Na_2O, up to about 8% ZrO_2 and up to about 2% MgO.

7. A method of forming a protective glaze surface on an architectural tile comprising:

providing a ceramic body;

applying a glaze composition to the ceramic body, the glaze composition comprising a zinc-free glass frit comprising, by weight, from about 50% to about 70% SiO_2, from about 5% to about 20% CaO, from about 3% to about 15% Al_2O_3, up to about 20% BaO, up to about 15% B_2O_3, up to about 10% K_2O, up to about 6% Na_2O, up to about 10% ZrO_2, up to about 5% MgO and up to about 5% PbO; and

firing the ceramic body to fuse the glaze composition to a surface thereof.

8. The method according to claim 7 wherein the applied glaze composition and ceramic body are co-fired during a single fast firing cycle at a temperature of from about 1080°C to about 1180°C.

9. The method according to claim 7 wherein the glaze composition is applied to the ceramic body after the ceramic body has been once-fired, and wherein the applied glaze composition and the once-fired ceramic body are co-fired during a second firing in a double fast firing cycle at a temperature of from about 1000°C to about 1150°C.

10. The method according to claim 7 wherein the glaze composition and the ceramic body are co-fired in a *gres porcellanato* ceramic firing cycle at a temperature of from about 1160°C to about 1250°C.

11. The method according to claim 7 wherein:

the zinc-free glass frit comprises BaO;

an ink composition comprising Cr^{+3} ions is applied to the applied glaze composition prior to firing; and

a yellow coloration develops in the protective glaze surface where the ink was applied and fired.

12. The method according to claim 7 wherein:

the zinc-free glass frit comprises BaO;

a conventional ink composition for decorating ceramic products is applied to the applied glaze composition prior to firing; and

a coloration develops in the protective glaze surface.